

### Remarks

In light of the above amendments and the following remarks, reconsideration of Claims 1-4 and their allowance are respectfully requested.

The specification has been amended to correct typographical and language/translation issues. The “M” and “T” effects have been defined as resonance or mesomeric effects and inductive effects respectively. These terms are well known to those skilled in the art as evidenced by the attached discussions in the textbooks “Organic Chemistry” by Morrison and Boyd and in “Physical Organic Chemistry” by Isaacs. The objected to term “thiolate” has been deleted and “S-S” has been deleted so that the specification conforms to the claims.

In Claim 1, the misspellings noted by the Examiner have been corrected. Equal signs (=) have been replaced by the term “represents.” Definitions of  $R^1$ ,  $R^2$  and  $R^6$  have been amended to conform with the descriptions in the specification (p. 2 line 42 – p. 3 line 7; p. 4 lines 21-25). The groups –CN and –NO<sub>2</sub> have been deleted from  $R^3$ . The counter ion M<sup>+</sup> (Li, Na, K, Rb or Cs), as described at p. 3 line 35, has been added to formula (IIIa2). The general narrative style has been amended to a more conventional format.

In Claims 2-4, equal signs (=) have been replaced by the term “represents” and the language has been slightly altered. The dependencies of Claims 3 and 4 have been changed.

Claim 8 has been cancelled.

Claims 1-4 are now in this case.

Claims 1-4 stand rejected under 35 U.S.C. § 112 second paragraph for being indefinite and for failing to point out and distinctly claim the subject matter of the invention. The grammatical and idiomatic errors pointed out by the Examiner, in addition to several others, have been corrected and it is believed the claims now meet the requirements of 35 U.S.C. § 112 second paragraph.

Claims 1 and 2 stand rejected under 35 U.S.C. § 112 first paragraph for not being enabled when R<sup>3</sup> is –CN and –NO<sub>2</sub>. As suggested by the Examiner, this rejection is overcome with the removal of –CN and –NO<sub>2</sub> from the definition of R<sup>3</sup>.

Claim 8 has been rejected based on double patenting of the “same invention” as claimed in claim 1 of US Patent 7,488,828. With the cancellation of Claim 8, this rejection becomes moot.

Claims 1-4 stand rejected on the grounds of nonstatutory obviousness-double patenting in view of US Patent 7,488,828. This rejection is overcome by the accompanying terminal disclaimer under 37 C.F.R. § 1.321(c).

The specification has been objected to with respect to several typographical and language issues. The spelling of “pyridine” at p 1 line 17 has been corrected. The redundant “the” has been deleted at p. 1 line 18. The “M” and “T” effects at p. 1 line 21 have been defined as resonance or mesomeric effects and inductive effects respectively. These terms are well known to those skilled in the art as evidenced by the attached discussions in the textbooks “Organic Chemistry” by Morrison and Boyd and in “Physical Organic Chemistry” by Isaacs. At p. 1 line 41, “bond” has been corrected to read “bound.” The ambiguous term “thiolate” has been deleted.

The specification has also been objected to with respect to several technical issues. The Wittig or Horner precursors are defined on p. 2 as organic halides of formula aIII. To remove any ambiguity with respect to E represents S-S at p. 3 lines 25 and 32 and elsewhere, the term “S-S” has been deleted from the definition of E throughout the specification. The specification now conforms with the definition of E in Claim 1. The Examiner is correct that at page 8 the intermediate structures IV-3 and IV-4 which contain an additional OR<sup>1</sup> group, would not be present in the case of Wittig reagents prepared in aprotic solvent. However, such intermediates are indeed present in the case when Horner reagents are used in alcoholic solvents. One of ordinary skill in the art would realize that the intermediates IV are the kinds of compounds that can result from reaction paths B1 and B2. The kinds and amounts of intermediates IV would depend on the reagents and conditions employed.

In view of the above remarks and amendments, reconsideration of this application and its allowance are respectfully requested.

Respectfully submitted,  
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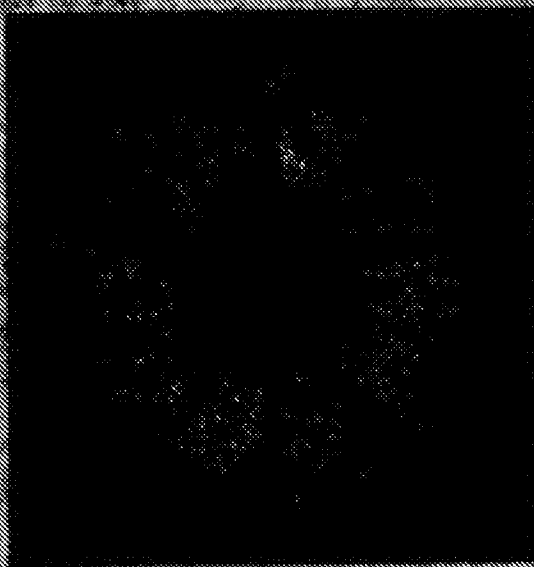
August 6, 2009

MORRISON  
AND BOYD

ORGANIC  
CHEMISTRY

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*Sixth Edition*



Library of Congress Cataloging-in-Publication Data

Morrison, Robert Thornton  
Organic chemistry / Robert Thornton Morrison. -- 6th ed.  
p. cm.  
Includes bibliographical references and index.  
ISBN 0-13-643669-2  
I. Chemistry, Organic. I. Boyd, Robert Neilson. II. Title.  
QD251.2.M67 1992 91-27444  
547—dc20 CIP

Acquisition Editor: *Diana Farrell*  
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*Cover photograph:* A computer-generated representation of DNA as viewed looking along the double helix. (Courtesy of the Computer Graphics Laboratory, University of California, San Francisco.  
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A Simon and Schuster Company  
Englewood Cliffs, New Jersey 07632

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Printed in the United States of America  
10 9 8 7 6 5 4 3 2

ISBN 0-13-643669-2

Prentice-Hall International (UK) Limited, *London*  
Prentice-Hall of Australia Pty. Limited, *Sydney*  
Prentice-Hall Canada Inc., *Toronto*  
Prentice-Hall Hispanoamericana, S.A., *Mexico*  
Prentice-Hall of India Private Limited, *New Delhi*  
Prentice-Hall of Japan, Inc., *Tokyo*  
Simon & Schuster Asia Pte. Ltd., *Singapore*  
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

Now, how does a substituent exert its polar effect? Despite the vast amount of work that has been done—and is still being done—on this problem, there is no general agreement, except that at least two factors must be at work. We shall consider electron withdrawal and electron release to result from the operation of two factors: the *inductive effect* and the *resonance effect*.

The **inductive effect** depends upon the "intrinsic" tendency of a substituent to release or withdraw electrons—by definition, its electronegativity—acting either through the molecular chain or through space. The effect weakens steadily with increasing distance from the substituent. Most elements likely to be substituted for hydrogen in an organic molecule are more electronegative than hydrogen, so that most substituents exert electron-withdrawing inductive effects: for example,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NO}_2$ .

The **resonance effect** involves *delocalization* of electrons—typically, those called  $\pi$  (pi) electrons. It depends upon the overlap of certain orbitals, and therefore can only operate when the substituent is located in certain special ways relative to the charge center. By its very nature, as we shall see (Sec. 11.14), the resonance effect is a stabilizing effect, and so it amounts to electron withdrawal from a negatively charged center, and electron release to a positively charged center.

The nature of the electron release by alkyl groups is not clear. It may be an inductive effect; it may be a resonance effect (*hyperconjugation*, Sec. 11.14), electrons being provided by overlap of  $\sigma$  bonds with the empty  $p$  orbital of the electron-deficient carbon. It may very well be a combination of the two. When we refer to the inductive effect of alkyl groups in this book, it should be understood that this may well include a contribution from hyperconjugation.

However it arises, the polar effect of alkyl groups is not a powerful one, as such effects go. Yet it leads to very large differences in stability among the various classes of carbocations. And it is these differences that we must keep uppermost in our minds in dealing with the varied chemistry of carbocations.

### 5.21 The $S_N1$ reaction: reactivity, Ease of formation of carbocations

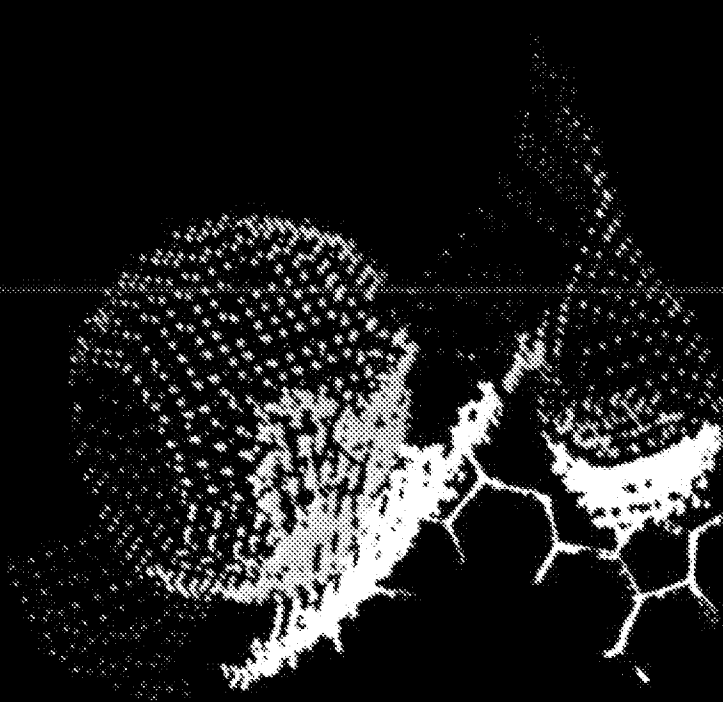
Once again let us return to nucleophilic substitution, and the matter of how the structure of the alkyl group affects reactivity. We have already seen (Sec. 5.14) that reactivity in  $S_N2$  decreases along the series  $\text{CH}_3\text{W}$ ,  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$ , as postulated by Hughes and Ingold (Sec. 5.11). Now, what are the facts with regard to the other half of their duality theory: does reactivity by  $S_N1$  change in the opposite direction along this same series?

Under conditions that greatly favor  $S_N1$ , results like the following have been obtained:

$S_N1$  substitution: relative reactivity



# Physical organic chemistry



**Neil S. Isaacs**

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**Longman Scientific & Technical**

Longman Group UK Limited  
Longman House, Burnt Mill, Harlow  
Essex CM20 2JE, England  
*and Associated companies throughout the world*

*Copublished in the United States with  
John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158*

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*First published 1987*

**British Library Cataloguing in Publication Data**

Isaacs, Neil S.

Physical organic chemistry.

1. Chemistry, Organic 2. Chemistry,  
Physical and theoretical

I. Title

547.1'3 QD476

ISBN 0-582-46366-1 ppr

ISBN 0-582-00474-8 csd

**Library of Congress Cataloging in Publication Data**

Isaacs, Neil S., 1934-

Physical organic chemistry.

Bibliography: p.

Includes index.

1. Chemistry, Physical organic. I. Title.

QD475.I846 1987 547.1'3 87-3848

ISBN 0-470-20787-6 (USA only)

Printed in Northern Ireland by  
The Universities Press (Belfast) Ltd.



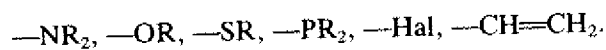
This is the benzene ring in the original Hammett systems and discussion will for the present center on benzenoid systems. Two basically distinct electronic effects may be generated by a substituent on a reaction site, and are discussed below.

#### 4.4.1 The resonance effect <sup>16</sup>

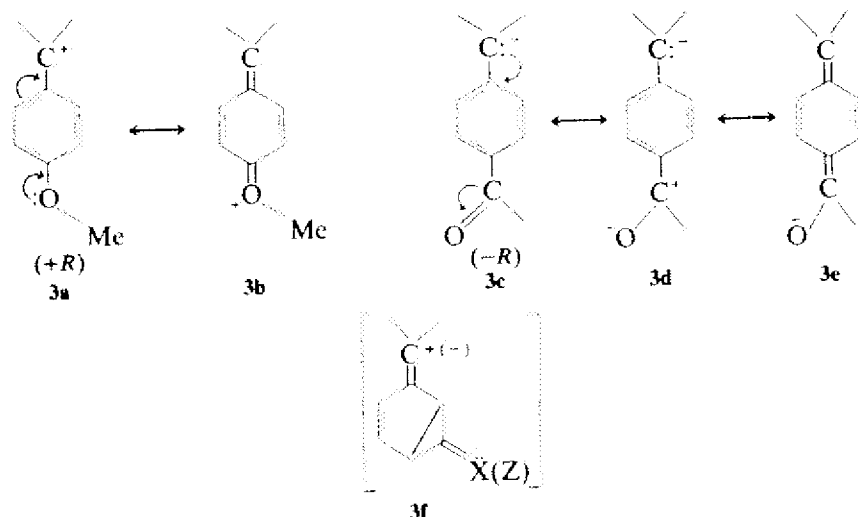
This is also known as the mesomeric effect, and is denoted *R*. Many substituents give rise to a perturbation which is greater when they are located *para* than when they are *meta*; this suggests the transmission mechanism is of a conjugative nature in which charge is relayed to alternate atoms. This effect is described here as a '+*R* effect' if it results in donation of electrons from substituent to reaction center and a '-*R* effect' if a withdrawal of electrons results. These effects would be characterized by negative and positive values of  $\sigma$ , respectively, so sign convention is slightly confusing.

In order to exercise a resonance effect, a substituent must possess a *p*- or  $\pi$ -orbital which is available to conjugate with the  $\pi$ -MOs of the aromatic system. Two situations are important.

(a)  $\ddot{X}$ - is a donor group and typically possesses an unshared electron pair or  $\pi$ -electrons on an atom directly attached to the ring. Examples are

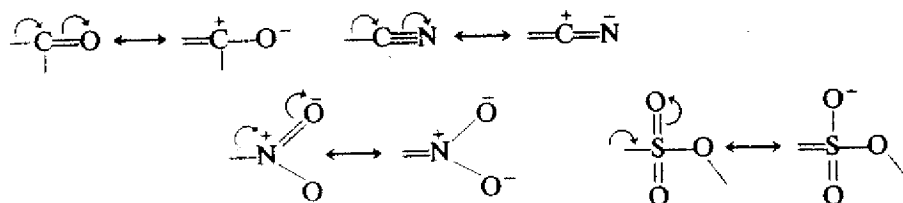


These groups are all capable of exerting a +*R* effect which stabilizes an acceptor center (e.g. a carbon bearing some degree of carbocation character) when in the *para* or *ortho* positions. The extreme situation is depicted by the VB structures, **3a**, **3b**. Little interaction between donor and



acceptor centers will occur if they are located *meta* since quinoid resonance structures analogous to **3b** and **3e** cannot be drawn and analogous structures (**3f**) are therefore of high energy and less important.

(b) Substituents Z have a  $\pi$ -acceptor center adjacent to the ring. Since no commonly encountered substituents possess vacant bonding *p*-orbitals, this means in practice groups which can act as electron acceptors by simultaneously releasing  $\pi$ -electrons to adjacent heteroatoms and whose VB contributing structures have a positively charged atom attached to the ring (**3c-e**). Common examples are



All such groups tend to accept electronic charge and stabilize donor centers (e.g. carbon bearing some degree of carbanion character adjacent to the ring), illustrated by contributing structure **3e**. Again, the strongest  $-R$  interactions occur when substituent and reaction centers are located *ortho* or *para* (**3e**).

It may be observed that there is no fundamental difference between these two situations; there is in each case a transfer of charge between two centers by conjugation and the differentiation into  $+R$  and  $-R$  effects merely depends upon which center we designate the substituent and which the reaction center.

#### 4.4.2 The inductive effect

The second type of perturbation evident from substituent constants results in the effect at the *meta* position being greater than that at the *para*. This is clearly observable in substituents such as  $-\text{NMe}_3$  (**4**) and  $-\text{CF}_3$  and depends for its strength upon proximity. This is called the inductive effect<sup>19,20</sup>, designated *I*;  $+I$  means electron-donating,  $-I$  electron-withdrawing. The basis of this electronic displacement is probably complex but originates in part from differences in electronegativity which cause

